



Effect of H₂O vapor addition on the photocatalytic oxidation of ethanol, acetaldehyde and acetic acid in the gas phase on TiO₂ semiconductor powders

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ABSTRACT

The effect of H₂O vapor addition on the photocatalytic oxidation of ethanol, acetaldehyde and acetic acid on TiO₂ semiconductor powders under UV light irradiation were investigated. The photocatalytic oxidation of acetaldehyde and acetic acid on TiO₂ surfaces was enhanced by the addition of H₂O vapor, its extent depending on the pressure while, on the other hand, the photocatalytic oxidation of ethanol was depressed by its coexistence with the H₂O vapor. Since the Ti⁴⁺ sites on the TiO₂ surfaces work as trap sites for the photo-formed electrons, the carbonyl compounds strongly adsorbed on the Ti⁴⁺ sites are not directly oxidized by the holes. However, when optimal amounts of H₂O molecules exist in the reaction system, the OH radicals formed by the photo-oxidation of H₂O molecules indirectly oxidize such organic species on the Ti⁴⁺ sites. In contrast, although ethanol molecules promptly interact with the photo-formed holes on the hydroxyl groups, the coexistence of H₂O molecules in the reaction system lessens the efficient interaction between ethanol and the hydroxyl groups on TiO₂ surfaces, resulting in a suppression of photocatalytic reactivity. In this way, the correlation of the different surface sites, such as Ti⁴⁺ or the hydroxyl groups, on which organic compounds adsorb and the photo-formed carriers are trapped, is not clearly understood but is observed to play an important role in the efficient photocatalytic oxidation of various organic compounds on TiO₂ semiconductor in the presence or the absence of an H₂O vapor.

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1. Introduction

In recent years, volatile organic compounds (VOCs), including formaldehyde, acetaldehyde, toluene and their derivatives, emitted from artificial building, adhesion and painting materials in newly built houses have caused debilitating damage to our health by the so-called “sick house syndrome”. TiO₂ has been widely studied as a photocatalyst to purify water, air and soil polluted with hazardous chemicals because of its high oxidative potential to completely decompose various organic compounds into harmless CO₂ and H₂O under UV light irradiation [1–4]. Moreover, it is believed that the degradation of such chemicals by TiO₂ photocatalysts is promoted in the presence of H₂O vapor. In many cases, the increase in photocatalytic reactivity by the addition of H₂O vapor can be explained by the decrease in the concentration of a persistent yet unreactive intermediate species accumulated on TiO₂ surfaces during UV light irradiation [5–10]. However, the adsorption states of the organic compounds on the TiO₂ surfaces are largely dependent on the kind of chemicals as well as the hydration states of the photocatalyst

surfaces [11,12]. As a result, the photocatalytic oxidation of organic compounds should greatly be affected by the surface environment or surface states of the TiO₂ photocatalysts such as the number of OH groups and Ti⁴⁺ cations. In addition, if some intermediate species with irritating and noxious odors or higher toxicity than the reactants desorb and diffuse in the gas phase during the photocatalytic reactions, more serious problems would arise. For example, since the vapor pressures of acetaldehyde (ca. 120 kPa at 298 K) is much higher than that of ethanol (7.88 kPa at 298 K), acetaldehyde readily diffuses into the gas phase as an intermediate during the photocatalytic oxidation of ethanol, resulting in expanded off-odor problems.

In this study, the photocatalytic oxidation reactions of ethanol, acetaldehyde and acetic acid over TiO₂ semiconductors under UV light irradiation were investigated. Moreover, the influence of H₂O vapor addition on the photocatalytic oxidation of these organic molecules with different properties have been discussed in detail from the viewpoint of the adsorption states of these molecules on TiO₂ photocatalyst surfaces.

2. Experimental

As the photocatalytic material, commercial TiO₂ powder (Degussa, P25; ca. 80% anatase and 20% rutile; SSA_{BET} = 50 m²/g;

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7–9 surface hydroxyls and ca. 3.5 H₂O molecules nm⁻² after outgassing at room temperature [13]) calcined at 673 K for 5 h was used.

The photocatalytic reactivity of the TiO₂ samples was evaluated by the oxidation of ethanol, acetaldehyde and acetic acid in the presence or absence of H₂O vapor under UV light irradiation in a closed system. The TiO₂ catalysts (50 mg) were first placed onto a flat bottom quartz cell (volume, ca. 33 cm³) connected to a vacuum line. Prior to photoreactions, all of the samples in the cell were outgassed at 723 K under high vacuum for 1.5 h, treated at the same temperature in O₂ atmosphere (ca. 6.67 kPa) and then outgassed under high vacuum at 373 K for 1.5 h. A gas mixture of C₂H₅OH, CH₃CHO or CH₃COOH (ca. 0.27 kPa), O₂ (ca. 1.07 kPa), and H₂O (0–1.33 kPa) was then introduced into the reaction cell. Before admission of these gases, the liquid samples were purified by several freeze–pump–thaw cycles. Since the volume of the reaction area was ca. 100 cm³, the amount of reactants in the cell was calculated as ca. 7 μmol (ca. 1500 ppm). After an adsorption equilibrium was reached, UV light was irradiated by a 100 W high-pressure Hg lamp (Toshiba, SHL-100UVQ-2) through a cutoff filter (Toshiba Glass, UV-27, λ > 270 nm). The production yield of CO₂ and residual organic compounds in the reaction cell were analyzed by a gas chromatograph (Shimadzu, GC-14A) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID).

The temperature programmed desorption (TPD) profiles of C₂H₅OH (the ratio of molecular weight [*m*] to charge carriers [*z*]; *m/z* = 46), CH₃CHO (*m/z* = 44) or CH₃COOH (*m/z* = 60) molecules adsorbed on the TiO₂ surfaces and ionized by high voltages of 1200 V, were monitored by a gas desorption analyzer (ANELVA, M-QA100TS) equipped with a quadrupole mass analyzer in a high-vacuum chamber of 10⁻⁹ kPa range [8]. The TiO₂ powder (30 mg) in the quartz cell was pretreated in the same way to the photoreactions while ethanol, acetaldehyde or acetic acid vapors were then adsorbed on the TiO₂ samples in the cell for 30 min. Before TPD measurements, the residual molecules in the cell were outgassed at room temperature for 1 h. TPD profiles were recorded by linear heating of the samples from 323 to 973 K at a constant rate of 5 K/min. The vapor pressures of C₂H₅OH, CH₃CHO and CH₃COOH at 298 K were 7.87, 120, 2.11 kPa, respectively.

The FT-IR spectra were recorded in the transmittance mode by a FT-IR spectrophotometer equipped with a DTGS detector (JASCO, FT-IR 660 Plus, resolution 4 cm⁻¹). The TiO₂ powder sample was pressed into a self-supporting pellet (apparent density ca. 10 mg/cm²) and placed in an in situ IR cell equipped with CaF₂ windows. UV light irradiation was carried out by a conventional 500 W super high-pressure Hg lamp (Ushio, USH-500BY) and guided by a fiber scope which focused on the pellet placed in the IR cell connected with a vacuum line (10⁻⁷ kPa range).

The diffuse reflectance UV–vis absorption spectra of TiO₂ under UV light irradiation in the presence of ethanol, acetaldehyde, acetic acid or H₂O vapors were measured. TiO₂ powder (150 mg) in an in situ quartz cell was pretreated in the same way for the photoreactions and the reactant vapors were then admitted onto the TiO₂ samples. After an adsorption equilibrium was obtained, UV light was irradiated onto the samples. After a certain period of irradiation time, the UV–vis absorption spectra of the TiO₂ samples were recorded in the diffuse reflectance mode by a spectrophotometer equipped with an integrating sphere (Shimadzu, UV-2200A, baseline calibration: BaSO₄).

3. Results and discussion

The influence of H₂O vapor addition on the photocatalytic oxidation of ethanol, acetaldehyde and acetic acid under UV light irradiation is shown in Fig. 1. The photocatalytic oxidation reac-

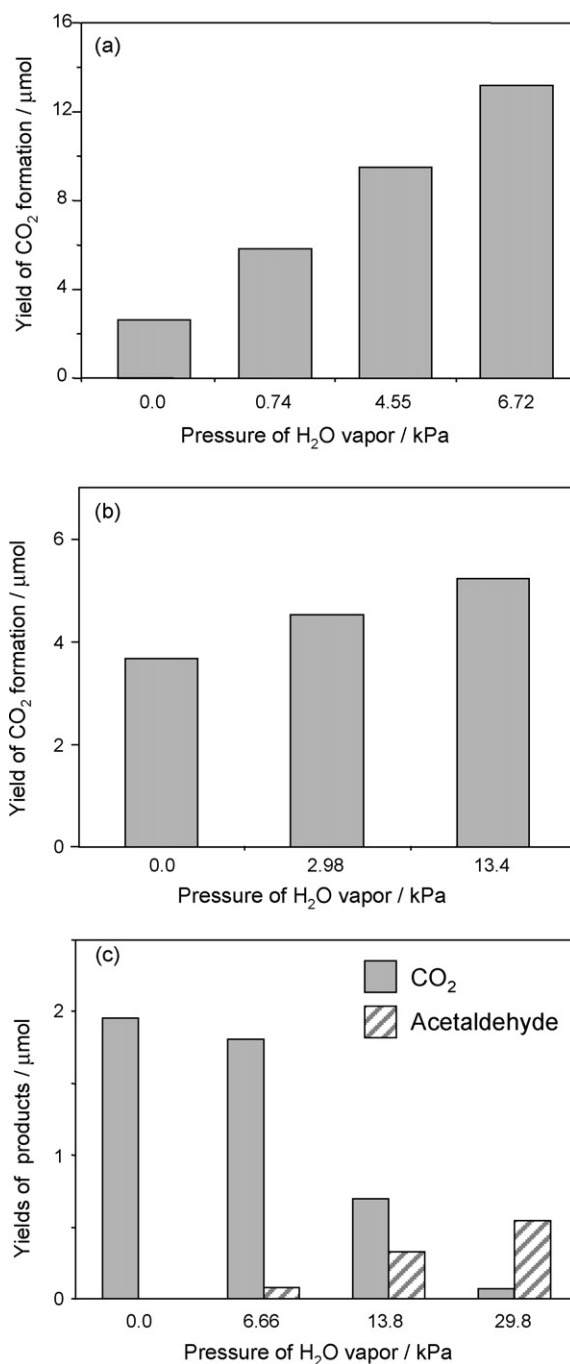


Fig. 1. Effect of H₂O vapor addition on the photocatalytic oxidation of: (a) acetaldehyde (6.8 μmol), (b) acetic acid (6.8 μmol) and (c) ethanol (6.8 μmol) with O₂ (28 μmol) on TiO₂ (Degussa P25, 50 mg) under UV light irradiation (λ > 270 nm). UV light irradiation time: (a) 3 h, (b) 1 h and (c) 0.5 h.

tivity of acetaldehyde was quite low in the absence of H₂O vapor but was dramatically enhanced by small amounts of its addition. In the case of acetic acid, the photocatalytic reactivity was slightly increased by the addition of H₂O vapor, while the photocatalytic oxidation reactivity of ethanol was depressed by its addition. Furthermore, no other by-product except for CO₂ and H₂O could be detected in the photocatalytic oxidation of acetaldehyde or acetic acid. However, when the photocatalytic oxidation of ethanol was carried out in the presence of H₂O vapor, acetaldehyde molecules as well as CO₂ could be detected in the gas phase. The time profiles of the photocatalytic oxidation of ethanol in the absence or presence of H₂O vapor are shown in Fig. 2. When H₂O vapor did not

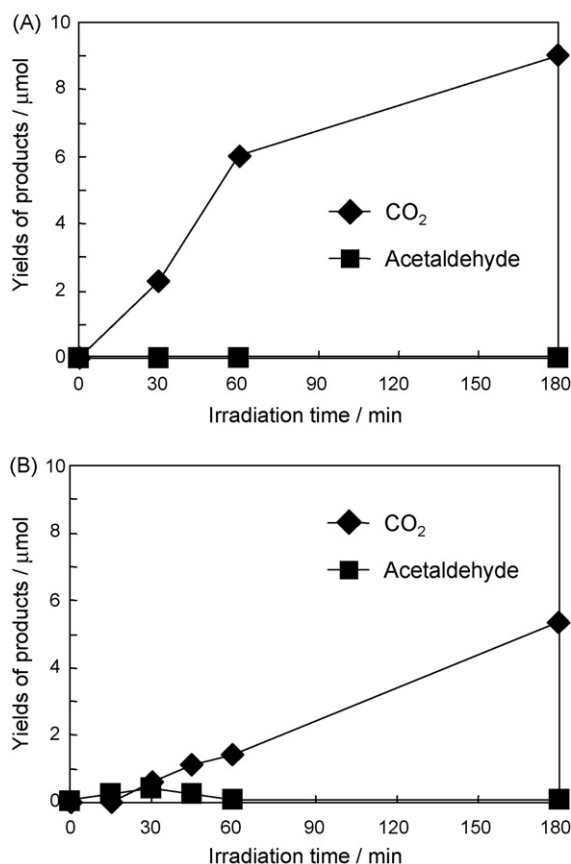


Fig. 2. Time courses of the photocatalytic oxidation of ethanol (6.8 μmol) with O_2 (28 μmol) on TiO_2 (Degussa P25, 50 mg) under UV light irradiation ($\lambda > 270 \text{ nm}$) in the (A) absence and (B) presence of H_2O vapor (13.3 kPa).

exist in the reaction system, the TiO_2 photocatalyst could efficiently decompose ethanol into CO_2 and H_2O under UV light irradiation without producing any other by-products. In contrast, when the H_2O vapor of ca. 13 kPa was added to the reaction system, the photocatalytic reactivity to oxidize ethanol decreased to half that in the absence of H_2O vapor. In addition, the formation of acetaldehyde as a by-product could be confirmed only in the initial stage of the photocatalytic reaction. These results clearly suggest that when ethanol in air is treated by an air purification system with defective and insufficiently reactive photocatalysts, ethanol is only partially oxidized into acetaldehyde and discharged into the air to cause displeasing or irritating odors since organic compounds must be efficiently and completely oxidized into CO_2 and H_2O for such a system to be effective.

The effect of H_2O vapor addition on the photocatalytic oxidation of ethanol, acetaldehyde and acetic acid are summarized in Fig. 3. When H_2O vapor did not exist in the reaction system, ethanol was easily decomposed, yet acetaldehyde was hardly decomposed on the TiO_2 photocatalyst. However, the addition of H_2O vapor in the reaction system was found to enhance the photocatalytic oxidation of acetaldehyde and acetic acid although the photocatalytic oxidation of ethanol drastically decreased. These results clearly indicate that the optimum photocatalytic oxidation of acetaldehyde or acetic acid should be carried out under humidified and moisturized conditions, while the photocatalytic oxidation of ethanol should be carried out under dehumidified conditions in the absence of any moisture.

In order to discuss the reason why the addition of H_2O vapor affects the photocatalytic oxidation of organic compounds, the difference in interactions between ethanol, acetaldehyde and acetic

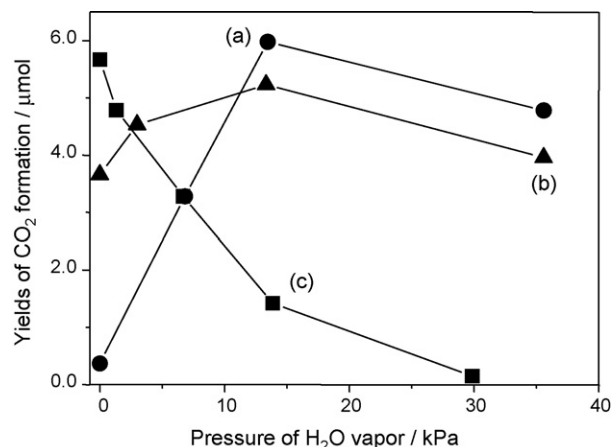


Fig. 3. Summary of the effect of H_2O vapor addition on the photocatalytic oxidation of: (a) acetaldehyde, (b) acetic acid and (c) ethanol with O_2 on TiO_2 under UV light irradiation for 1 h.

acid molecules with the TiO_2 surface was investigated by TPD measurements, as shown in Fig. 4. The desorption of ethanol ($m/z = 46$) or acetic acid ($m/z = 60$) molecules from the TiO_2 surfaces was mainly observed at temperatures lower than 523 K. The $-\text{OH}$ moieties of ethanol or acetic acid molecules weakly interact with the hydroxyl groups of the TiO_2 surfaces via the hydrogen bonds. Since the surface hydroxyl groups work as trap sites for the photo-formed holes, the organic species weakly adsorbed on the hydroxyl groups can directly be oxidized by the holes. In contrast, desorption of the acetate ions ($m/z = 59$) or acetaldehyde ($m/z = 44$) molecules could be observed in relatively higher temperatures of 523–723 K. As reported in previous literature [8], the desorption of acetaldehyde can be distinguished from that of CO_2 by analyzing the desorption profiles of fragments such as CH_3 ($m/z = 15$), CHO ($m/z = 29$), and CH_3CO ($m/z = 43$). Generally, the acetate anions or the carbonyl groups of aldehyde molecules strongly interact with the Ti^{4+} sites of the TiO_2 surfaces by nucleophilic interactions [6,8,14–19]. Furthermore, since such cation sites of the TiO_2 surfaces can work as trap sites for the photo-formed electrons, the organic species interacting with the Ti^{4+} sites are not directly decomposed by the holes which are trapped on the surface hydroxyl groups. In this case, the organic species strongly adsorbed on the Ti^{4+} sites may indirectly be decomposed by the OH radicals that are formed by the oxidation of H_2O molecules by the photo-formed holes. Such a contribution of

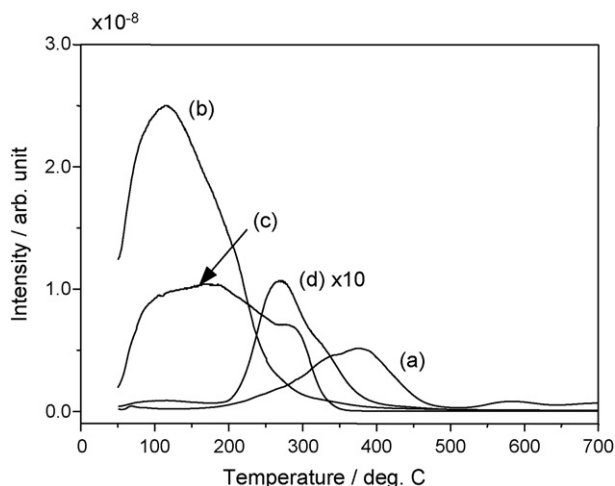


Fig. 4. TPD profiles of: (a) acetaldehyde ($m/z = 44$), (b) acetic acid ($m/z = 60$), (c) ethanol ($m/z = 46$) and (d) acetate ions ($m/z = 59$) adsorbed on TiO_2 surfaces.

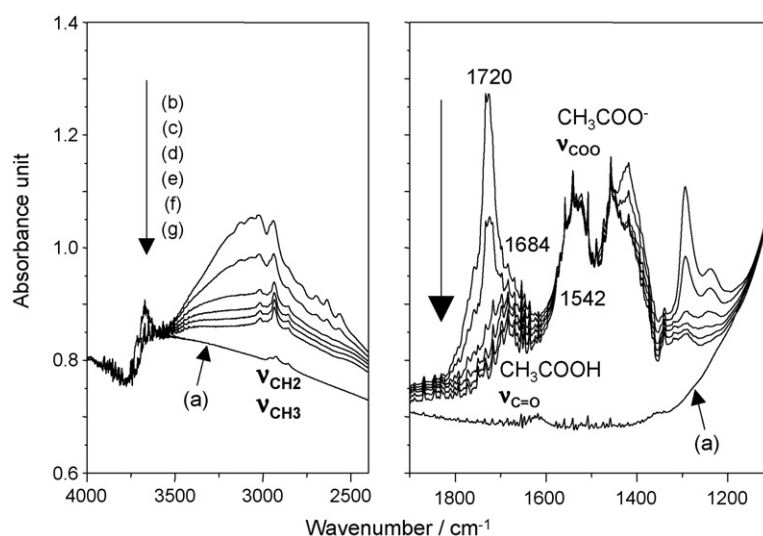


Fig. 5. FT-IR spectra of the acetic acid molecules and acetate ions adsorbed on TiO₂ surfaces: (a) after pretreatment at 723 K (background), (b) adsorption of CH₃COOH (2.11 kPa), (c–g) outgassed at room temperature after (b) until the pressure in the FT-IR cell reached lower than 0.75, 0.16, 0.022, 6.7×10^{-4} , and 1.2×10^{-4} kPa, respectively.

the OH radicals to the oxidation reaction can explain the enhancement in the photocatalytic oxidation of acetaldehyde or acetic acid in the presence of H₂O vapor.

The adsorption, desorption as well as photodegradation processes of acetic acid on the TiO₂ photocatalyst surfaces were investigated by FT-IR measurements. When the TiO₂ surfaces pretreated at 723 K were exposed to acetic acid vapor of ca. 2.1 kPa at room temperature, the absorption bands assigned to the CH₃COO[−] (acetate) ions adsorbed on the Ti⁴⁺ sites and CH₃COOH in the gas phase could be observed at 1600–1400 and 1720 cm^{−1}, respectively [6,15,20–21]. As shown in Fig. 5, the absorption band at 1720 cm^{−1} due to the CH₃COOH molecules in the gas phase readily decreased by degassing at room temperature and the small absorption band due to the weak interactions of the CH₃COOH molecules with the surface hydroxyl groups could be observed at 1684 cm^{−1}. On the other hand, the acetate ions at 1600–1400 cm^{−1} hardly decreased by degassing at room temperature. It is known that acetate ions strongly adsorb onto the cation sites of oxide surfaces by nucleophilic interactions [14–21].

As shown in Fig. 6A, when the TiO₂ surfaces adsorbed with two different species, such as the CH₃COOH molecules weakly adsorbed on the hydroxyl groups and the CH₃COO[−] ions strongly adsorbed on the Ti⁴⁺ sites, were irradiated by UV light, the methyl and carbonyl groups of the CH₃COOH molecules on the surface hydroxyl groups promptly decreased. At the same time, formation of H₂O molecules could be observed at around 3600–3000 cm^{−1}. However, the CH₃COO[−] ions on the Ti⁴⁺ sites slowly decreased as compared to CH₃COOH molecules. The changes in peak intensities attributed to the CH₃COOH molecules (1684 cm^{−1}), CH₃COO[−] ions (1542 cm^{−1}) and H₂O molecules (3400 cm^{−1}) are plotted in Fig. 6B. Almost all of the CH₃COOH molecules showing weak interactions with the surface hydroxyl groups were decomposed in the early stages of UV light irradiation. In contrast, it was observed that the CH₃COO[−] ions strongly adsorbed on the Ti⁴⁺ cation sites gradually decomposed and small amounts of acetate ions existed on the TiO₂ surfaces even after UV light irradiation of 30 h.

In the photocatalytic reactions, the photo-formed electrons are generally consumed by O₂ while the photo-formed holes are consumed by H₂O or organic molecules. When TiO₂ photocatalysts are irradiated with UV light in the presence of only organic molecules, the photo-formed holes on the TiO₂ surfaces are promptly consumed by the reaction with the organic compounds while the photo-formed electrons remain without any reactions and accumu-

late on the TiO₂ surfaces, changing the electronic state and resulting in a color change to blue-gray. The blue-gray color assigned to the photo-reduced TiO₂ surfaces can be observed as a broad absorption in visible to infrared light regions [22–25]. In order to discuss

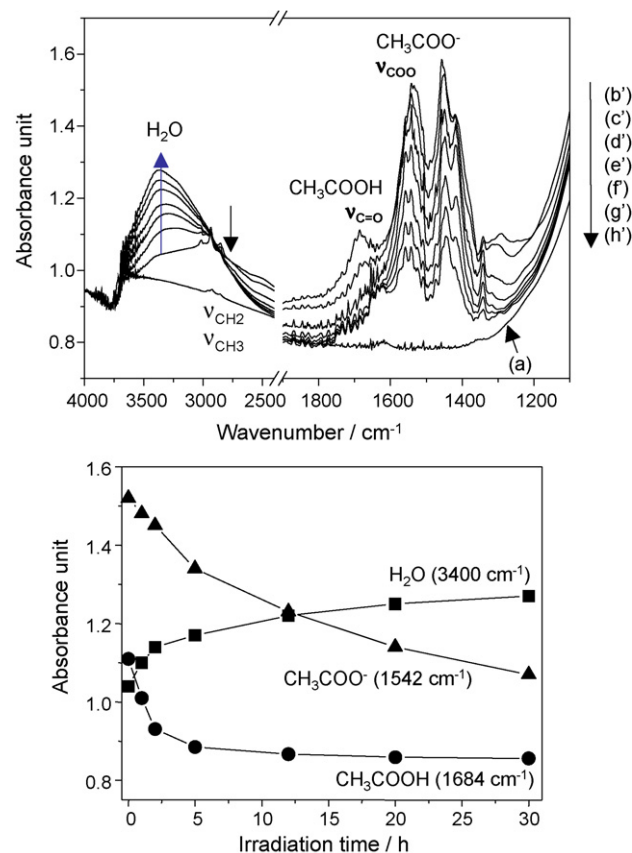


Fig. 6. (A) FT-IR spectra in the process of photocatalytic oxidation of acetic acid molecules and acetate ions adsorbed on the TiO₂ surfaces with O₂ under UV light irradiation: (a) after pretreatment at 723 K, (b') after adsorption of CH₃COOH (2.11 kPa), CH₃COOH in the gas phase was outgassed, pressure in FT-IR cell: 1.2×10^{-4} kPa [Fig. 5(g)], and (c'–h') under UV light irradiation for 1, 2, 5, 12, 20 and 30 h. (B) Time courses of the peak intensities of CH₃COOH (1684 cm^{−1}), CH₃COO[−] (1542 cm^{−1}) and H₂O (3400 cm^{−1}) adsorbed on the TiO₂ surfaces under UV light irradiation.

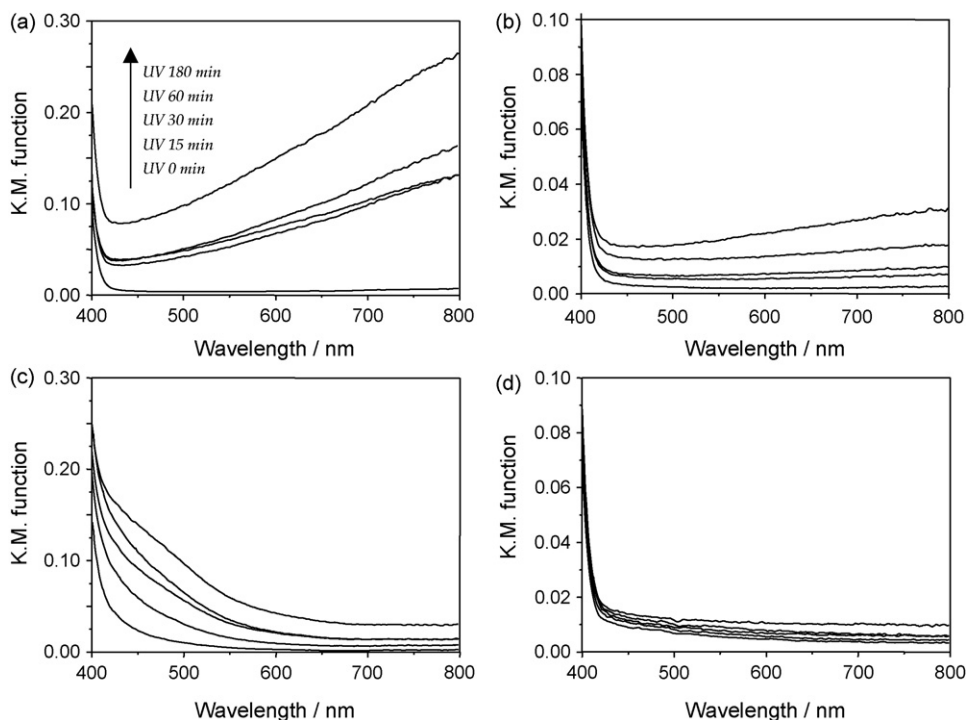


Fig. 7. Diffuse reflectance UV–vis absorption spectra of the TiO_2 adsorbed with (a) ethanol, (b) H_2O , (c) acetaldehyde and (d) acetic acid under UV light irradiation ($\lambda > 270 \text{ nm}$). UV light irradiation time (from bottom to top): 0, 15, 30, 60 and 180 min.

the different interactions between the organic molecules and the photo-formed holes, the effect of UV light irradiation on the absorption spectra of the TiO_2 photocatalysts in the presence of various organic molecules were investigated, as shown in Fig. 7. The time courses in the absorption intensities at 800 nm are also summarized in Fig. 8. When the TiO_2 powders were irradiated with UV light in the presence of ethanol vapor, broad absorption in visible light regions dramatically increased. In the case of H_2O vapor, absorption in visible light regions increased to some extent. These results clearly show that ethanol or H_2O molecules are promptly oxidized by the photo-formed holes trapped on the surface hydroxyl groups. In contrast, when the TiO_2 powders were irradiated with UV light in the presence of acetaldehyde or acetic acid vapors, absorption in visible light regions hardly increased. However, UV light irradiation on TiO_2 surfaces in the presence of acetaldehyde led to

a color change of the TiO_2 catalysts from white to pale yellow, indicating the accumulation of some organic compounds such as polyaldehyde on the catalyst surfaces. These results clearly indicate that acetaldehyde or acetic acid molecules hardly interact with the photo-formed holes. In the photocatalytic production of H_2 from H_2O , methanol is generally used as a sacrificial reagent [26,27]. This fact may also explain the interaction of alcohol molecules with the hydroxyl groups of the photocatalyst surface and which consume the photo-formed holes, resulting in the efficient reduction of H^+ into H_2 . From this viewpoint, carbonyl compounds were found to be unsuitable as sacrificial reagents for photocatalytic H_2 production. These phenomena are explained by the contribution of the additional decomposition of the carbonyl compounds which are strongly adsorbed on the photo-formed electron trap sites by the OH radicals originating from the photo-oxidation of the H_2O molecules. Moreover, since H_2O molecules generally adsorb on cation sites as well as surface hydroxyl groups, enhancement of the photocatalytic oxidation of acetaldehyde or acetic acid by the addition of H_2O vapor can be explained by the decrease in the persistent adsorption species on the Ti^{4+} cation sites. In contrast, the depression of the photocatalytic oxidation of ethanol by the addition of H_2O vapor can be explained by the competitive adsorption of H_2O and ethanol molecules onto the surface hydroxyl groups.

In order to discuss the amount of acetic acid molecules weakly adsorbed on the TiO_2 surfaces, the TiO_2 samples adsorbed with enough amounts of acetic acid were outgassed at 473 K. The desorption amount of the molecularly adsorbed acetic acid from the surface hydroxyl groups could be confirmed at approximately 70–75% by GC analysis. The acetate ions strongly adsorbed on the Ti^{4+} sites could then be roughly estimated at 25–30%. The TiO_2 samples adsorbed with acetate ions were irradiated with UV light in the presence of only H_2O vapor. Although the yield of CO_2 production was quite low, these results clearly indicate that the acetate ions on the Ti^{4+} sites were gradually decomposed by the OH radicals originating from the photo-oxidation of H_2O molecules.

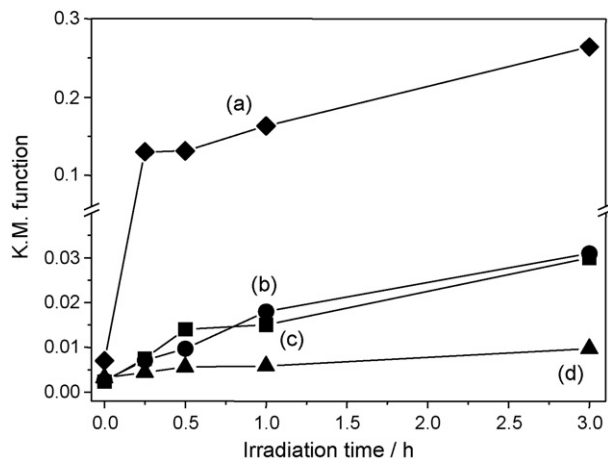


Fig. 8. Time courses of the absorption intensities at 800 nm in the DR UV–vis absorption spectra of the TiO_2 adsorbed with: (a) ethanol, (b) H_2O , (c) acetaldehyde and (d) acetic acid under UV light irradiation ($\lambda > 270 \text{ nm}$).

4. Conclusions

The photocatalytic oxidation of ethanol, acetaldehyde and acetic acid molecules with O₂ on TiO₂ semiconductor powders under UV light irradiation were found to be greatly affected by the addition of H₂O vapor. Since acetaldehyde and acetic acid molecules, especially acetate ions, containing a carbonyl group strongly adsorb on the Ti⁴⁺ sites to trap the photo-formed electrons, these organic species are hardly decomposed by the photo-formed holes trapped on the surface hydroxyl groups. The photocatalytic oxidation of carbonyl compounds were enhanced in the presence of H₂O vapor, indicating that these organic species on the Ti⁴⁺ sites are indirectly decomposed by the OH radicals formed by the photo-oxidation of H₂O molecules. On the other hand, the photocatalytic oxidation of ethanol with O₂ on TiO₂ surface was suppressed by the addition of H₂O vapor. Since H₂O and ethanol molecules competitively adsorb on the hydroxyl groups of TiO₂ surfaces, the existence of H₂O molecules inhibits efficient interactions between the ethanol molecules and photo-formed holes on the hydroxyl groups. In this way, the optimal conditions, especially humidity controls, for the efficient oxidation of various organic compounds on TiO₂ semiconductor photocatalysts were investigated.

References

- [1] N. Serpone, E. Pelizzetti (Eds.), *Photocatalysis Fundamentals and Applications*, Wiley, New York, 1989.
- [2] D.F. Ollis, H. Al-Ekabi (Eds.), *Photocatalytic Purification and Treatment of Water and Air*, Elsevier, Amsterdam, 1993.
- [3] M. Anpo, H. Yamashita, in: M. Schiavello (Ed.), *Heterogeneous Catalysis*, Wiley, London, 1997.
- [4] A. Fujishima, K. Hashimoto, T. Watanabe (Eds.), *TiO₂ Photocatalysis Fundamentals and Applications*, BKC, Tokyo, 1999.
- [5] L. Liao, W. Wu, C. Chen, J. Lin, *J. Phys. Chem. B* 105 (2001) 7678.
- [6] G. Martra, S. Coluccia, L. Marchese, V. Augugliaro, V. Loddo, L. Palmisano, M. Schiavello, *Catal. Today* 53 (1999) 695.
- [7] J. Fan, J. Yates Jr., *J. Am. Chem. Soc.* 118 (1996) 4686.
- [8] M. Takeuchi, T. Kimura, M. Hidaka, D. Rakhmawaty, M. Anpo, *J. Catal.* 246 (2007) 235.
- [9] J.M. Coronado, M.E. Zornl, I. Tejedor-Tejedor, M.A. Anderson, *Appl. Catal. B: Environ.* 43 (2003) 329.
- [10] M. Zhang, T. An, J. Fu, G. Sheng, X. Wang, X. Hu, X. Ding, *Chemosphere* 64 (2006) 423.
- [11] M. Takeuchi, L. Bertineti, G. Martra, S. Coluccia, M. Anpo, *Appl. Catal. A: Gen.* 307 (2006) 13.
- [12] M. Takeuchi, G. Martra, S. Coluccia, M. Anpo, *J. Near Infrared Spectrosc.* 17 (2009) 373.
- [13] G. Munuera, V. Rives-Arnau, A. Saucedo, *J. Chem. Soc., Faraday Trans. 1* (75) (1979) 736.
- [14] M.A. Henderson, *J. Phys. Chem. B* 101 (1997) 221.
- [15] B.E. Hayden, A. King, M.A. Newton, *J. Phys. Chem. B* 103 (1999) 203.
- [16] H. Onishi, Y. Iwasawa, *Chem. Phys. Lett.* 226 (1994) 111.
- [17] Q. Guo, I. Cocks, E.M. Williams, *J. Chem. Phys.* 106 (1997) 2924.
- [18] H. Uetsuka, A. Sasahara, A. Yamakata, H. Onishi, *J. Phys. Chem. B* 106 (2002) 11549.
- [19] H. Uetsuka, H. Onishi, M.A. Henderson, J.M. White, *J. Phys. Chem. B* 108 (2004) 10621.
- [20] J. Ryczkowski, *Catal. Today* 68 (2001) 263.
- [21] Z. Yu, S.S.C. Chuang, *J. Catal.* 246 (2007) 118.
- [22] D. Bahnemann, A. Henglein, J. Lilie, L. Spanhel, *J. Phys. Chem.* 88 (1984) 709.
- [23] R.F. Howe, M. Grätzel, *J. Phys. Chem.* 89 (1985) 4495.
- [24] T. Berger, M. Sterrer, O. Diwald, E. Knözinger, D. Panayotov, T.L. Thompson, J.T. Yates Jr., *J. Phys. Chem. B* 109 (2005) 6061.
- [25] M. Takeuchi, G. Martra, S. Coluccia, M. Anpo, *J. Phys. Chem. C* 111 (2007) 9811.
- [26] K. Domen, J.N. Kondo, M. Hara, T. Takata, *Bull. Chem. Soc. Jpn.* 73 (2000) 1307.
- [27] S. Fukumoto, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, *Catal. Lett.* 127 (2009) 39.